

CLAIMS

1. A process for the preparation of phenol comprising the following phases:
 - 1) preparation in continuous of phenol by means of the direct oxidation of benzene with hydrogen peroxide operating with an H₂O₂/benzene ratio ranging from 10 to 70%, in a three-phase reaction system comprising a first liquid phase consisting of benzene and an organic solvent, a second liquid phase consisting of water, a solid phase consisting of an activated catalyst based on titanium silicalite TS-1;
 - 2) separation of the phenol and non-reacted benzene from the reaction mixture of the oxidation section (1), by means of fractionated distillation;
 - 3) separation of the solvent and by-products consisting of benzenediols from the mixture coming from the distillation tail (2), by means of basic extraction;
 - 20 4) transformation of the by-products obtained in section (3) to phenol by means of hydrodeoxygenation with hydrogen operating in continuous, in aqueous solution, at a temperature ranging from 250 to 500°C, at pressures of 1-100 bar and in the presence of a catalyst based on elements of group VIB

or their mixtures or group VIII of the periodic table or their mixtures;

5) recycling of the phenol obtained in section (4) to the distillation section (2).

5 2. The process according to claim 1, wherein the direct oxidation of benzene is carried out in a three-phase reaction system comprising a quantity of water ranging from 5 to 50% by weight with respect to the reaction mixture.

10 3. The process according to claim 2, wherein the water is present in a quantity ranging from 15 to 40%.

4. The process according to claim 1, wherein the direct oxidation of benzene is carried out in a three-phase reaction system comprising an organic solvent consisting of sulfolane, in quantities ranging from 20 to 80% by weight with respect to the reaction mixture.

15 5. The process according to claim 4, wherein the sulfolane is present in quantities ranging from 40 to 70%.

20 6. The process according to claim 1, wherein the direct oxidation of benzene with hydrogen peroxide is carried out in the presence of a catalyst based on titanium silicalite TS-1 selected from those having general formula (I);

wherein: x ranges from 0.0001 to 0.04, preferably from 0.02 to 0.03, in quantities ranging from 2 to 60% by weight with respect to the benzene, activated by means of a pretreatment with fluorine ions and hydrogen peroxide.

- 5 . 7. The process according to claim 6, wherein the catalyst is present in quantities ranging from 5 to 40% by weight with respect to the benzene.
- 10 . 8. The process according to claim 1, wherein the direct oxidation is carried out in quantities of benzene ranging from 10 to 80% by weight with respect to the reaction mixture.
- 15 . 9. The process according to claim 8, wherein the direct oxidation is carried out in quantities of benzene ranging from 15 to 50% by weight with respect to the reaction mixture.
- 20 . 10. The process according to claim 1, wherein the oxidation reaction is carried out at temperatures ranging from 50° to 110°C.
- 20 . 11. The process according to claim 10, wherein the oxidation reaction is carried out at temperatures ranging from 70° to 100°C.
- 25 . 12. The process according to claim 1, wherein the by-products consisting of benzenediols which are transformed into phenol are in aqueous solution at a con-

centration of 5-60% by weight.

13. The process according to claim 12, wherein the benzenediols are in aqueous solution at a concentration of 10-40% by weight.

5 14. The process according to claim 1, wherein the hydrode-oxygenation is effected with hydrogen operating with a molar ratio with respect to the benzenediols of 2-50.

15. The process according to claim 14, wherein a molar ratio of 5-30 is adopted with respect to the benzenediols.

10 16. The process according to claim 1, wherein the hydrode-oxygenation is carried out in the presence of a catalyst based on elements of group VIB and a promoter selected from elements belonging to group VIII and phosphorous.

15 17. The process according to claim 16, wherein the catalyst based on elements of group VIB is selected from molybdenum and tungsten and the promoter is selected from nickel, cobalt, iron and ruthenium.

20 18. The process according to claim 1, wherein the hydrode-oxygenation is carried out in the presence of a catalyst based on elements of group VIII selected from cobalt, palladium, nickel and platinum and a promoter selected from zinc, rhenium, selenium, tin, germanium and lead.

19. The process according to claim 1, wherein the hydrode-oxygenation is carried out in the presence of a catalyst deposited on a carrier.
20. The process according to claim 19, wherein the carrier
5 is selected from alumina, silica, titanium dioxide, crystalline or amorphous alumino-silicates, crystalline spinels having the general formula $F^{2+}R_2^{3+}O_4$, wherein F^{2+} is selected from Mg, Fe, Zn, Mn, Ni, and R^{3+} is selected from Al, Fe, Cr or their mixtures.
- 10 21. The process according to claim 16 and 19, wherein the hydrodeoxygenation is carried out in the presence of a catalyst based on an element of group VIB deposited on a carrier at a concentration ranging from 1 to 50% by weight and a promoter at a concentration ranging from
15 0.1 to 100% atomic with respect to the element of group VIB.
22. The process according to claim 18 and 19, wherein the hydrodeoxygenation is carried out in the presence of a catalyst based on an element of group VIII deposited
20 on a carrier at a concentration ranging from 0.05 to 20% by weight and a promoter at a concentration ranging from 0.5 to 200% atomic with respect to the element of group VIII.